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Project Title: **Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation**

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Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation

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Research Objective: The Department of Energy's nuclear complex contains a significant amount of contaminated concrete containing radionuclides only in the near-surface region, typically a few millimeters deep. DOE will realize significant savings in decontamination costs and waste volume if the contaminated surface is removed from the clean bulk. Laser ablation is attractive because it adds no additional waste, offers fine control over the amount of material removed, can work on cracked, curved or irregular surfaces, can potentially be instrumented for real-time analysis, and can be used on virtually any material surface. The objectives of this research are to determine the mechanism and efficacy of laser ablation in removing contaminated surface layers, to understand the chemistry of contaminated concrete surfaces, and to chemically and physically characterize the captured ablation effluent which would become the stored waste. While the focus of this project is on concrete, the technology should be applicable to any surface requiring removal.

Research Progress and Implications: This report summarizes work after 20 months of a three-year project. Ablation experiments were done with a 1.6 kW pulsed Nd:YAG laser. The beam was delivered via a fiber optic cable, focused at or near the surface, and rastered. The virgin and ablated surfaces and ablation effluent were chemically and physically characterized. In addition, optical emission spectra were obtained on-line during the laser ablation process itself.

Rather than defining a set of operating parameters specific to our laser systems, our studies are geared toward revealing the fundamental ablation mechanisms, i.e. the processes by which optical energy removes material from the surface, and the fate of contaminants after ablation. In addition, we have worked to find the optimal speed and efficiency for the process in terms of the amount of material removed per unit optical energy per unit time. These results can be applied to other lasers in order to design an optimal ablation system for a given need. The intent is to learn how to use lasers as tools to do various jobs.

Concrete is a complex heterogeneous material containing phases encompassing many size scales and chemical compositions. We have shown that several different ablation mechanisms exist simultaneously when concrete is ablated at high power with a pulsed laser. The most important in terms of bulk material removal is the shock wave created by differential thermal expansion during rapid heating by the laser pulse, which causes most aggregate material (such as sand or rock) to fracture into small pieces (up to a few millimeters in diameter) and explode off the surface. Since sand and aggregate typically make about 90% of the bulk of high density concrete, the overall ablation rate is dominated by this process. The overall removal rate depends on several factors, such as laser power, pulse repetition rate, laser raster rate, focused spot diameter, and focal position with respect to the surface. In general, high power, fast raster rates and large beam diameters lead to the highest removal rates. The ablation efficiency (mass removed per unit energy delivered to the surface) is relatively unaffected by parameters such as total power or focused spot size. Efficiency does drop as raster rates slow and consecutive pulses overlap significantly because the residual heat left in the matrix by previous pulses lowers the thermal gradient created by the latest pulse and leads to melting rather than an explosion of the material. In addition, it was noted that the efficiency rose by up to 20% when the laser was focused either just above or just below the surface. We are currently investigating this phenomenon.

The cement portion of the concrete comprises only about 10% of the total, but is important because it is the phase in which the bulk of the contamination resides. Cement can melt, spatter, vaporize, and/or disaggregate (i.e. explode) depending on the intensity and duration of the laser pulse. The laser-melted or -vaporized cement forms an aerosol which can have a very different chemical composition than the virgin cement. The aerodynamic particle size distribution, as determined by a particle impactor, was bimodal. The distribution was peaked at the high (8.5 µm) and low (<0.5 µm) ends and had a minimum at about 1 µm. This suggests that particles form by two mechanisms, namely vaporization/condensation for small particles and melt/spatter for large particles. This interpretation is bolstered by energy dispersive spectroscopy, which showed that small particles had disproportionately large concentrations of aluminum compared to both the larger particles and the virgin cement, suggesting that small particles formed by condensation from vapor, with an aluminum-rich nucleating phase. The cesium and strontium concentrations in the aerosol were also strongly correlated with particle size. Neutron activation analysis (NAA) showed that particles with aerodynamic diameters below 0.5 µm were enriched in cesium by up to a factor of two compared to the virgin cement, while larger particles were substantially depleted in cesium. In contrast, particles in the aerodynamic size range from 0.5 to 1.6 µm - the smallest of those formed by melt/spatter - were enriched in strontium by up to a factor of two over the virgin cement, while all others were depleted. The NAA data is consistent with the proposed particle formation mechanisms. Since cesium is very volatile compared to the other elements in the cement, it should be distilled out of the melted material and appear in the particles formed from the vapor phase. Strontium is less volatile and tends to remain with the melted/spattered fraction, though the reason for its preferential precipitation in the smaller of the melted particles is unclear.

Laser desorption mass spectrometry (LDMS) of cesium- and strontium-doped Portland cement and high density concrete samples showed that cesium resides in the adsorbed water in the cement pores (the “pore water”), while strontium resided in the cement matrix itself. LDMS analysis of ablated samples also demonstrated the potential for decontamination by laser ablation. A sample of the exterior surface of a sample of high density concrete exposed to an aqueous solution of CsCl was shown to have a 30- to 300-fold reduction of Cs after removal of 0.6 to 0.8 mm of material after a single high-power laser ablation pass.

Optical emission spectra of the ablation plume (i.e. the hot gasses produced by the laser-surface interaction) were collected and analyzed. A number of peaks were easily assigned to cesium and strontium, as well as many of the cement matrix elements. The high power and long pulse duration of the industrial Nd:YAG make it especially well suited to this type of analysis and offer the possibility of on-line analysis for a number of elements.

Planned Activities: Laser ablation studies will be extended to higher power and the effect of pulse duration will be investigated. We will also compare the performance of Nd:YAG and CO_2 lasers to assess the effect of wavelength on the ablation efficiency and mechanisms. We will continue to investigate the use of laser-induced breakdown spectroscopy in this application.

Information Access:

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3. “Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation,” Pellin, M.J.; Savina, M.R.; Reed, C.B.; Wang, Y.; Xu, Z., Presented at Characterization, Monitoring and Sensing Workshop, Gaithersburg, MD, March, 1999, http://infoshare.inel.gov/EMSP/wkshop/cmst/laser.pdf
4. “Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation,” Savina, M.R.; Pellin, M.J.; Leong, K; Xu, Z., Presented at EMSP Workshop, Rosemont, IL, July, 1998, http://www.doe.gov/em52/1998posters/id60283.pdf